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Study on the interaction of anionic dye–nonionic surfactants in a mixture of anionic and nonionic surfactants by absorption spectroscopy

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Abstract

The interaction between an anionic dye C.I. Reactive Orange 16 (RO16) and different surfactants, i.e., the anionic surfactant sodium dodecylsulfate (SDS) and nonionic surfactants polyoxyethylene ethers (C_mPOE_n; $m = 12$, 16 and 18, $n = 4$, 10 and 23) has been researched spectrophotometrically in a certain micellar concentration range. Light absorbances in the visible spectral range are measured as a function of mole fraction of surfactant at four different temperatures and at 24 h over the periodic time intervals. For this reason, a typical system occurred at 1.0×10^{-2} mol/l for surfactants and at 1.0×10^{-4} mol/l for dye concentrations. It is evident from the experimental measurements that while nonionic surfactants form a complex with the anionic dye RO16 in aqueous solution in studied concentration range, anionic surfactant does not. The formation of C_mPOE_n–RO16 complex in the SDS solutions of different mole fractions in its micellar concentration range has been determined and compared to those obtained in the dye–surfactant binary mixtures. Spectrophotometric measurements indicated that the value of absorbance of SDS–RO16 is greater than that of nonionic surfactant–RO16 in the binary systems. This state explains that the ionic and hydrophobic interactions between SDS–RO16 are less than that of nonionic surfactant–RO16 interactions. The addition of SDS to the mixture of C_mPOE_n–RO16 causes an increase in the value of absorbance. This increase is due to changed hydrophobic–hydrophilic balance of the studied mixtures. Furthermore, we observed that the alkyl chain length and the number of polyoxyethylene in nonionic surfactants do not have an enormous effect on the values of absorbance.

Keywords: Spectrophotometry; Dye–surfactant interaction; Anionic dye; Anionic–nonionic surfactant

1. Introduction

Although a lot of research work has already been done in dye–surfactant interaction, the studies in this area are still important and interesting for the theory and technology of dyeing. Surfactants are used as solubilizers for water insoluble dyes, to break down dye aggregates in order to accelerate adsorption processes on fiber, as auxiliaries for improving dye adsorption and as levelling or dispersing agents [1–4]. In practice, mixtures of surfactants are used because a single surfactant rarely satisfies all requirements. On the other hand, some phenomena which are not expected to take place in the single system occur in the aqueous solution containing surfactant mixtures [5–8]. For the mixture of two surfactants undergoing micelle formation above a critical micelle concentration (CMC), the solution properties fall either between or outside the solution properties of the two single-surfactant solutions [9]. Mixed surfactant systems are also known to exhibit synergism or antagonism, leading to enhanced performance properties. The phenomenon of synergism is due

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to the interaction between the different head groups. On the other hand, antagonism can be reached by mixing surfactants with some kinds of head groups, but different kinds of chains, one hydrocarbon and the other perfluorinated [10].

It would be interesting to study a mixed system that contains an anionic dye and an anionic surfactant with similar hydrophilic groups but different hydrophobic parts. In such a system, mixed micelle formation should be mainly due to the hydrophobic effect of the alkyl chains and steric restrictions because there is almost no favorable interaction between the charged groups. In general, nonionic surfactants interact strongly with anionic surfactant but weakly with cationic surfactant. This is interpreted to be due to the bulkiness of the cationic head group, to a more favorable interaction between anionic surfactants [11,12]. In a previous study, we were concerned with the surface adsorption and micelle formation of the mixture of sodium dodecylsulfate (SDS) and polyoxyethylene 23 lauryl ether (Brij 35). We found the value of interaction parameter between SDS and Brij 35 by using Rubing's Theory [13]. In the present study, we studied an anionic dye–nonionic surfactants interaction in the absence and presence of SDS by spectrophotometric method. UV/VIS spectrophotometric measurements have been carried out for binary and ternary RO16–surfactant mixed systems at 30, 35, 40 and 45 °C and at 24 h over the periodic time intervals. We also discussed optimum conditions for surfactants and temperatures used in the colour fastness of anionic dye.

2. Experimental

2.1. Materials

2.1.1. Anionic surfactant

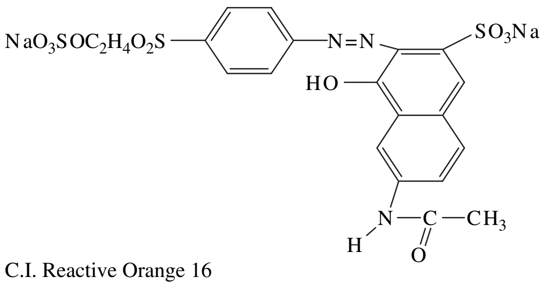
Sodium dodecylsulfate (SDS) ($C_{12}H_{25}OSO_3^-Na^+$) was supplied by Merck with 98% purity. It was extracted with ether, recrystallized from ethanol followed by drying under vacuum.

2.1.2. Nonionic surfactants

Alkyl polyoxyethylene ethers (C_mPOE_n, $m = 12$, 16 and 18, $n = 4$, 10 and 23) were supplied by Sigma.

2.1.3. Anionic dye

C.I. Reactive Orange 16 (RO16) was purchased from DyStar and used as received. It exhibits a maximum absorption band (1.577) at 494 nm and 25 °C. The purity of the surfactants used was further confirmed by the absence of minima in the surface tension against the logarithm of the concentration curve. Water used in the preparation of the solutions was distilled twice from dilute alkaline permanganate solution; its conductivity was about 1.0×10^{-6} S cm^{-1}and air/water tension was equal to 71–72 m Nm^{-1} at 25 °C.



C.I. Reactive Orange 16

2.2. Methods

2.2.1. CMC measurements

The surface tension of aqueous solutions of single and mixed surfactants at various concentrations was measured using the Du Nouy ring method at certain temperatures. The CMC values were determined at sharp break points in surface tension against the logarithm of the concentration curve. In addition, the CMC values were found to be in agreement with measured specific conductivity and density. These CMC values were found to be 8.0×10^{-3} for SDS and between 4.0×10^{-5} M ($C_{12}POE_4$) and 9.5×10^{-4} M ($C_{16}POE_{10}$) for nonionic surfactants at 25 °C. From the surface tension measurement, we observed that within the temperature range of 25–50 °C, the value of CMC of pure surfactants did not vary whereas the value of CMC of mixed surfactant decreases as temperature increases above 25 °C. Therefore, it was selected from a wide concentration range.

2.2.2. Preparation of mixed surfactant solutions

Using CMC values which were found for each surfactant solution, a certain total concentration (1.0×10^{-2} M) was selected. At this selected concentration, micellization was present for all surfactant solutions, and so stock solutions were prepared at this concentration. As dye concentration, 1.0×10^{-4} M concentration value which exhibits a maximum absorption band (1.577) at 494 nm was found from calibration curve. Dye–surfactant mixed systems were prepared as mole fraction of nonionic surfactants and total surfactant concentration and dye concentration was taken hold of stable. Prepared solutions were placed in 100 ml Erlenmeyers and shaken for 96 h in a thermostat bath at four different temperatures. The absorbance values of these solutions were measured at 24 h periodic time intervals.

2.2.3. Spectrophotometric measurements

The absorbance measurements of dye–surfactant solutions were carried out at four temperatures by

Shimatzu UV-160A spectrophotometer which had two quartz cells (10.0 mm in light pass length).

3. Results and discussion

Fig. 1 shows the change of the value of absorbance of RO16 at 494 nm with time for various mole fractions of SDS in SDS–$C_{12}POE_{23}$ mixed surfactant system at 35 °C. As seen from Fig. 1, the values of absorbance of dye in the studied solutions are lower than that of dye at the selected concentration (1.0×10^{-4} mol/l). This suggests that dye–surfactant and surfactant–surfactant interactions exist in all the studied solutions. The value of absorbance in $C_{12}POE_{23}$ was lower in comparison to that of the dye in SDS and dye alone (for $C_{12}POE_{23}$: 1.482, for SDS: 1.536, for dye: 1.577). This explains that there are more strong interactions between RO16 and nonionic surfactants. In the solution, RO16–$C_{12}POE_{23}$ interaction can be explained by ionic interaction between the sulfonic groups of dye and the oxonium species of the nonionic surfactant [14,15] and hydrophobic interaction between hydrophobic alkyl chains of surfactants with the hydrophobic portion of dye [16,17]. By means of these interactions, the complex occurs between RO16 and nonionic micelles of $C_{12}POE_{23}$. In dye–nonionic mixed surfactant system, the value of absorbance decreasing with time is explained using the stability of RO16–$C_{10}POE_{23}$ complex increasing with time.

It can also be observed that the value of absorbance of dye increased in the presence of SDS. In this case (over a range of 0.2–0.8 mole fraction) which contains three components SDS, RO16 and $C_{12}POE_{23}$ in the solution, it was considered that SDS anions interact with both the species, dye anions and $C_{12}POE_{23}$ micelles. In the SDS–RO16 interaction, there are interaction repulsive electrostatic interactions between similar hydrophilic groups and hydrophobic interaction between alkyl chains of dye and SDS, so RO16 very slightly solubilizes in SDS micelles but remained in the water phase. Therefore, the increase of the value of absorbance in solution obtained by adding SDS can be attributed to the attractive forces between anionic head groups of SDS and oxonium ions of nonionic surfactant and hydrophobic interaction between alkyl chains of the two surfactants. It was previously reported that in nonionic surfactants consisting of POE groups, oxonium ions are formed in the hydrophilic portion of surfactant [18]. Desai and Dixit have shown that the repulsion exists between the cationic head group and oxonium ions of nonionic surfactant in mixed micelle [19]. The interaction between SDS–$C_{12}POE_{23}$ creates counter-balance against RO16–$C_{12}POE_{23}$ and so the value of absorbance remains almost constant with time. At SDS–RO16 binary system (1.0 mole fraction of SDS), there is hydrophobic interaction between hydrophobic groups of dye and SDS. As mentioned above, the value of absorbance of dye has changed very slightly, and is independent of time.

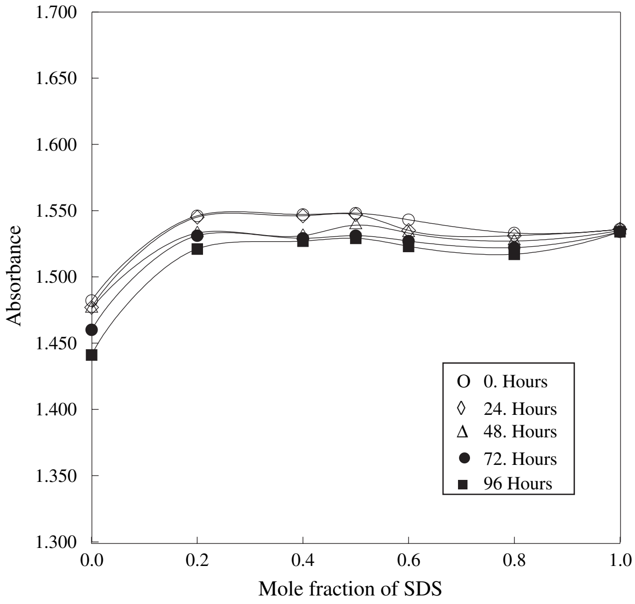


Fig. 1. The relationship between the values of absorbance of RO16 and mole fraction of SDS at five periodic time intervals in SDS–$C_{12}POE_{23}$ mixed surfactant system at 35 °C. Total surfactant concentration is 1.0×10^{-2} mol/l.

The changes in the absorbance of RO16 at various mole fractions of SDS at four different temperatures after shaking for 48 h are shown in Fig. 2. As seen from the figure, the temperature has no effect on the absorbance of ternary and SDS–RO16 binary systems. Also in the SDS–RO16 system, the value of absorbance slightly changes with temperature. As reported by Karlstrom, POE became less polar as the temperature increased [20], and so the decrease in polarity reduces hydrophilic interaction but this interaction is balanced with hydrophobic interaction between alkyl chains of dye and SDS.

Fig. 3 depicts the effect of ethylene oxide groups on the value of absorbance of RO16 in the SDS–$C_{12}POE_n$ ($n = 4$, 10 and 23) mixed surfactant systems by the mole fraction of SDS at 35 °C and after shaking for 48 h. The effect of the alkyl chain length on the value of absorbance in SDS–C_mPOE_{10} ($m = 12$, 16 and 18) mixed surfactant system at the above mentioned conditions is shown in Fig. 4. As can be seen in both systems, the values of absorbance of dye do not vary enormously with increasing ethylene oxide number and alkyl chain length. Since the interactions between anionic and nonionic surfactants are strong in the ternary systems, dye–nonionic interactions are balanced with the hydrophilic–hydrophobic interactions.

The change in the value of absorbance of dye is a measure for the extent of interaction. The largest

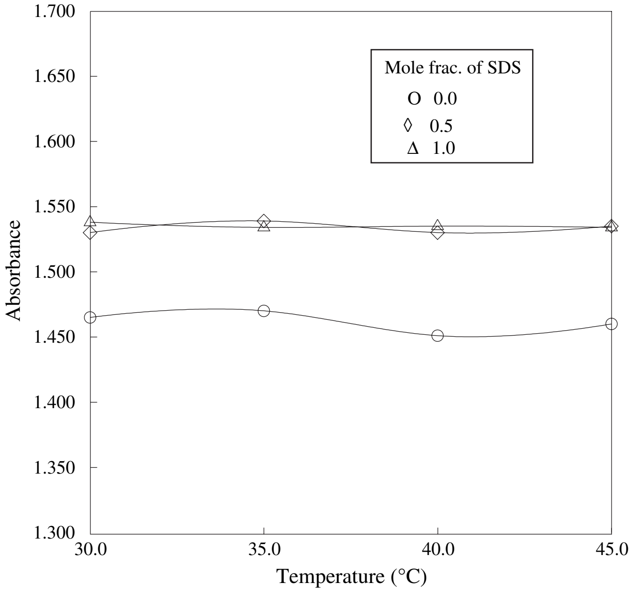


Fig. 2. The effect of temperature on the values of absorbance of RO16 in SDS–$C_{12}POE_{23}$ mixed surfactant system with various mole fractions after shaking for 48 h. Total surfactant concentration is 1.0×10^{-2} mol/l.

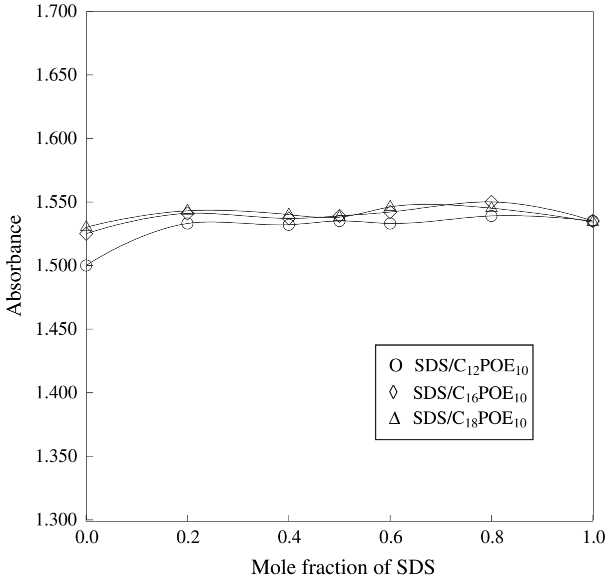


Fig. 4. The effect of alkyl chain length on the absorbance of RO16 in the SDS–C_mPOE_{10} ($m = 12$, 16 and 18) mixed surfactant systems at 35 °C for various mole fraction of SDS. Total surfactant concentration is 1.0×10^{-2} mol/l.

decrease of value of absorbance which represents more interactions, is observed in the C_mPOE_n–RO16 mixed systems. The extent of the complex formation can be decreased with the addition of SDS. In the RO16–SDS–C_mPOE_n ternary systems, the value of absorbance is independent of temperature, the number of ethylene oxide and alkyl chain length. It is evident that mixture of surfactants is used as a levelling agent in the dye solutions [21].

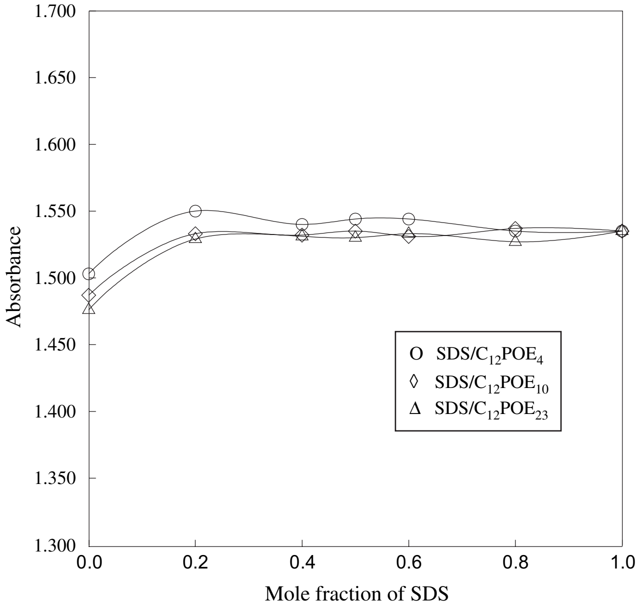


Fig. 3. The effect of a number of ethylene oxide groups on the absorbance of RO16 in the SDS–$C_{12}POE_n$ ($n = 4$, 10 and 23) mixed surfactant systems at 35 °C for various mole fraction of SDS. Total surfactant concentration is 1.0×10^{-2} mol/l.

Acknowledgment

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